

REMARKS

In the Office Action, claims 27-29, 36, 40-44 and 46 are rejected under 35 U.S.C. § 102; claims 30, 31, 38, 39, 48, 49, 51 and 52 are rejected under 35 U.S.C. § 103; and claims 32-35, 37, 45, 47 and 50 have been objected to. Claims 27 and 30 have been amended, claims 53-60 have been newly added, and claims 29, 31-35, 37, 45, 47 and 50 have been canceled without prejudice or disclaimer. Applicants believe that the rejections have been overcome for at least those reasons set forth below.

At the outset, claims 32-35, 37, 45, 47 and 50 are objected to but would be allowable if rewritten in independent form. See, Office Action, page 5. In response, Applicants have added claims 53-60. Claim 53 essentially incorporates the limitations of claim 27 and claim 32 and any intervening claims; claim 54 essentially incorporates the limitations of claim 27 and claim 33 and any intervening claims; claim 55 depends from claim 54 and further adds the limitation as defined in claim 34; claim 56 essentially incorporates the limitations of claim 27 and claim 35 and any intervening claims; claim 57 essentially incorporates the limitations of claim 27 and claim 37 and any intervening claims; claim 58 essentially incorporates the limitations of claim 40 and claim 45 and any intervening claims; claim 59 essentially incorporates the features of claim 40 and claim 47 and any intervening claims; and claim 60 essentially incorporates the features of claim 40 and claim 50 and any intervening claims. Claims 32-35, 37, 45, 47 and 50 have been canceled without prejudice or disclaimer as previously discussed. Thus, Applicants believe that newly added claims 53-60 should be rendered allowable.

With respect to the anticipation and obviousness rejections, the Patent Office primarily relies on WO 94/04461 (Withers). In support of the obviousness rejection, the Patent Office further relies on the Kiang et al. reference. See, Office Action, page 4. Applicants believe that the anticipation and obviousness rejections are improper.

Of the pending claims at issue claims 27 and 40 are the sole independent claims. Claim 27 recites a method for producing fullerene. The method includes providing a pair of carbon-based electrodes that are spaced apart to define a region therebetween; generating an arc discharge between the pair of carbon-based electrodes; and supplying a gas containing carbon to the region between the electrodes. Claim 27 has been amended to further recite that the gas containing carbon includes a hydrocarbon gas and sulfur and thus effectively represents claim 31

in independent form which has been cancelled without prejudice or disclaimer. Claim 40 recites a device for producing fullerene. The device includes a pair of carbon rod electrodes; and a gas supply mechanism that is capable of continuously supplying gas containing carbon to a region spaced between the pair of carbon rod electrodes.

In contrast, Applicants believe that the cited art even if combinable is distinguishable from the claimed invention. For example, nowhere does the primary Withers reference disclose or suggest the arc discharge of a gas containing carbon between a pair of carbon-based electrodes to produce fullerenes. Indeed, the primary focus of Withers relates to an arc vaporization process. See, Withers, page 8. Contrary to the Patent Office's position, Fig. 13a in Withers illustrates how a suitable hydrocarbon in particulate form can be fed between the tips of electrodes 101a, 102a where the arc causes the carbon from the hydrocarbon to be vaporized. The vaporized carbon is then quenched by the surrounding inert gas atmosphere and condensed and collected within the reactor 103. See, Withers, page 23, line 14 to page 24, line 3. This clearly contrasts the claimed invention that recites, in part, the arc discharge of a gas containing carbon between a pair of carbon-based electrodes to form fullerenes.

Further, Withers does not disclose the use of sulfur. As previously discussed, Claim 27 has been amended to further recite that the gas containing carbon includes a hydrocarbon gas and sulfur. Therefore, Applicants believe that Withers on its own is distinguishable from the claimed invention for at least these reasons.

In addition, Applicants do not believe that the Patent Office can rely solely on the Kiang reference to remedy the deficiencies of Withers. Indeed, the Patent Office merely relies on Kiang for its purported use of methane, sulfur, and a catalyst to form carbon nanotubes. See, Office Action, page 4. Further, nowhere does Kiang disclose the use of gaseous sulfur to promote the production of nanotubes contrary to the Examiner's assertion. See, Office Action, page 4. Rather, Kiang discloses that sulfur was incorporated in the form of either cobalt sulfide (CoS) or elemental S mixed with the Co and graphite powders in the anode. See, Kiang, page 6614. Kiang teaches that a hole is drilled in the anode and the Co compound containing sulfur is packed into the hole. See, Kiang, page 6612. Thus, Applicants believe that the teachings of Kiang are insufficient in scope and detail to cover the claimed invention, even if combinable with Withers.

Based on at least these reasons, Applicants believe that the cited art is distinguishable from the claimed invention. Therefore, Applicants respectfully submit that the cited art, even if combinable, fails to anticipate and render obvious the claimed invention.

Accordingly, Applicants respectfully request that the anticipation and obviousness rejections be withdrawn.

Applicants note for the record that the reference CN 1273286A dated November 15, 2000 which was cited in Applicants' previously filed Information Disclosure Statement is attached hereto as Exhibit A. This is in response to the Patent Office's comments regarding the resubmission of this reference for consideration during examination of this case. See, Office Action, page 2. Therefore, Applicants respectfully request that this reference be considered during the examination of this case and that the Patent Office indicate as such by providing Applicants with an initialed copy of PTO 1449 form indicating same. If the Patent Office should have any questions regarding this request, Applicants respectfully request that the Patent Office contact the undersigned attorney directly in an attempt to bring a prompt resolution to this matter.

For the foregoing reasons, Applicants respectfully submit that the present application is in condition for allowance and earnestly solicit reconsideration of the same.

Respectfully submitted,

BELL, BOYD & LLOYD LLC

BY 

Thomas C. Basso
Reg. No. 46,541
P.O. Box 1135
Chicago, Illinois 60690-1135
Phone: (312) 807-4310

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[71] 申请人 中国科学院金属研究所
地址 110015 辽宁省沈阳市沈河区文化路 72 号
[72] 发明人 成会明 范月英 魏永良 吕曼琪
刘 敏 苏 革 沈祖洪

[74] 专利代理机构 中国科学院沈阳专利事务所
代理人 张 晨

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[54] 发明名称 一种纳米碳纤维储氢材料的制备方法

[57] 摘要

一种纳米碳纤维储氢材料的制备技术,制备出的纳米碳纤维直径在 5~200 nm,以苯、 CH_4 、 C_2H_2 为碳源,以二茂铁、 $\text{Ni}(\text{Co})_4$ 为催化剂,以氢、氨、氮气为载气,其特征在于:以含硫化合物如噻吩、 H_2S 为生长促进剂,并且控制碳源与载气的摩尔比在 0.08~0.18,碳与硫摩尔比为 700~1000:1,催化剂与碳源的摩尔比为 0.008~0.015;将含硫化合物碳氢化合物与催化剂在气态下充分混合,被载气匀速 带入反应区,在反应区中保留 0.5~0.075s,在 1373K~1473K 下生长纳米碳纤维。本发明可以制备出大量储氢量大、性能稳定的储氢材料,且该方法简便易行,适合工业化生产。

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说明书

一种纳米碳纤维储氢材料的制备方法

本发明涉及储氢材料,特别提供了一种具有超级储氢能力的纳米碳纤维材料的制备技术。

今天,在世界范围内普遍存在矿物能源短缺、环境污染严重等问题,人们迫切需求洁净的新能源。而氢能正以其独有的优势和丰富的资源引起人们广泛的兴趣。世界各国都在氢能的研究和开发上投入了大量的人力、物力。其中,氢的利用主要包括氢的生产、储存和运输、应用三个方面。而氢的储存是关键,储氢材料正是在这样的背景下产生的,并得以迅猛发展。

1886年美国现代化学奠基人Thamas Graham发现金属钯能够大量吸氢。一个世纪以后,直到1968年美国Brookhaven国立研究所率先在储氢合金的研究上获得成功,发现了 Mg_2Ni 合金也具有储氢性能。1970年荷兰菲利普研究所发现了 $LaNi_5$ 的储氢性能。与此同时,美国的Brookhaven国立研究所又发现了 $FeTi$ 储氢合金,从而揭开了储氢合金研究的新篇章。但是金属合金材料储氢量普遍很低,以研究较多、技术相对成熟的 $LaNi_5$ 为例,其饱和储氢量为1.4 wt%。加之金属合金材料具有比重大、循环吸氢过程中易出现枝晶和晶粒细化等缺点,无法满足汽车工业上要求单次充气行程远、循环寿命长和成本低的基本要求。Dillon等人对氢能汽车候选储氢系统储氢能力进行了系统比较,认为一台可行驶500 km的汽车需耗氢3.1 Kg,这要求系统储氢能力必须达到6.5 wt%。虽然液态氢和高压氢可达到此指标,但氢液化需消耗25~45%的氢能,压缩氢气到20 MPa需消耗9%的氢能而且很危险,其它体系如金属储氢远远不能满足实用要求。他们发现单壁纳米碳管可储氢约10 wt%,接近此目标,但大量制备单壁纳米碳管的方法还有待发展。因此,有必要重新寻找一种储氢量大而易制备的新型储氢材料。美国东北大学用基体法,利用不同的催化剂制备出直径在50 nm的三种结构的纳米碳纤维,如:石墨片层平行于纤维轴向的tubular型纳米碳纤维,其储氢量为11.26 wt%;石墨片层与纤维轴向呈一定角度的herringbone型的纳米碳纤维,其储氢量达到55 wt%;石墨片层垂直

于纤维轴向的platelet型纳米碳纤维,其储氢量达到45 wt%。但迄今为止未能有其它研究小组重复该结果。

本发明的目的在于提供一种纳米碳纤维储氢材料的制备技术,使用该方法可以制备出大量储氢量大、性能稳定的储氢材料,且该方法简便易行,适合工业化生产。

本发明提供了一种纳米碳纤维储氢材料的制备技术,制备出的纳米碳纤维直径在5~200 nm,以苯、 CH_4 、 C_2H_2 为碳源,以二茂铁、 $\text{Ni}(\text{Co})_4$ 为催化剂,以氢、氮、氦气为载气,其特征在于:以含硫化合物如噻吩、 H_2S 为生长促进剂,并且控制碳源与载气的摩尔比在0.08~0.18,碳与硫摩尔比为700~1000:1,催化剂与碳源的摩尔比为0.008~0.015;将含硫化合物碳氢化合物与催化剂在气态下充分混合,被载气匀速带入反应区,在反应区中保留0.5~0.075 S,在1373K~1473K下生长纳米碳纤维。

本发明中含硫化合物为噻吩,碳源为苯时,当噻吩溶于某溶液中,噻吩重量浓度0.05~1.0%,当含硫化合物为 H_2S 时, H_2S 进入反应区的量为0.5~1 ml/min。

本发明气相生长纳米碳纤维表面具有分子级细孔,内部具有直径大约10 nm的中空管,比表面积大,而且可以合成石墨层面垂直于纤维轴向或与轴向成一定角度的鲑鱼骨状特殊结构的纳米碳纤维,其层面间距为3.37 Å,远远大于氢分子直径(2.89 Å),因此,大量氢气可以在VGCNF中凝聚,从而具有超级储氢能力。实验表明100 nm左右碳纤维的储氢量可达到10~13 wt%。

下面通过实施例详述本发明。

附图1为纳米碳纤维设备示意图。

附图2为纳米碳纤维的储氢装置设备示意图。

附图3为纳米碳纤维的宏观照片。

附图4为纳米碳纤维的透射电子显微镜照片。

附图5为纳米碳纤维的高分辨照片。

实施例1

装置如附图1。

碳苯流量40 ml/min, 噻吩浓度为1%, 载气 H_2 总流量为600 ml/min, 催化剂为二茂铁, 重量为0.7 g。反应区先以25°C/min升至1100°C后, 再以15°C/min, 升至1200°C, 恒温45 min。

产品为块状, 有弹性。在扫描电子显微镜下观察, 所得产品纯净, 不含碳黑。在透射电子显微镜观察, 可以清楚地看到中空管的存在。直径分布也比较均匀, 其直径范围为80~100nm。

实施例2

装置如附图1。

碳 CH_4 流量240 ml/min, H_2S 流量为0.5 ml/min, 载气 H_2 总流量为550 ml/min, 催化剂为二茂铁, 重量为0.6 g。反应区先以25°C/min升至1100°C后, 再以15°C/min, 升至1200°C, 恒温45 min。

产品为块状, 有弹性, 见图3。在扫描电子显微镜下观察, 所得产品纯净, 不含碳黑。在透射电子显微镜观察, 可以清楚地看到中空管的存在。纳米碳纤维的直径分布也比较均匀, 其直径范围为100nm。

实施例3

将气相生长纳米碳纤维用盐酸浸泡除铁后, 用蒸馏水冲洗, 直至呈中性。将冲洗好的纳米碳纤维放入烘箱中在100°C下烘干。然后将纳米碳纤维放入储氢实验设备的样品室内。将样品室置于恒温水浴或加热炉在100~150°C下抽真空5小时, 然后储氢。

装置如附图2。

取大约125 nm的气相生长纳米碳纤维用酒精分散后, 用37%浓HCl浸泡, 再用去离子水冲洗。将冲洗好的纳米碳纤维置于烘箱中烘干。再放入储氢装置的样品室中, 在150°C下抽真空3小时。纳米碳纤维的储氢量为10.01 wt%。

实施例4

装置如附图2。

取大约100 nm的气相生长纳米碳纤维用酒精分散后, 用37%浓HCl浸泡, 再用去离子水冲洗。将冲洗好的纳米碳纤维置于烘箱中烘干。再放入储氢装置的样品室中, 在100°C下抽真空5小时。纳米碳纤维的储氢量为10.03 wt%。

实施例5

装置如附图2。

取大约90 nm的气相生长纳米碳纤维用37%浓HCl浸泡,再用去离子水冲洗。将冲洗好的纳米碳纤维置于烘箱中烘干。再放入储氢装置的样品室中,在100℃下抽真空5小时。纳米碳纤维的储氢量为12.82 wt%。

实施例6

装置如附图2。

取大约80 nm的气相生长纳米碳纤维没有经过处理直接放入储氢装置的样品室中,在100℃下抽真空5小时。纳米碳纤维的储氢量为12.38 wt%。

说明书附图

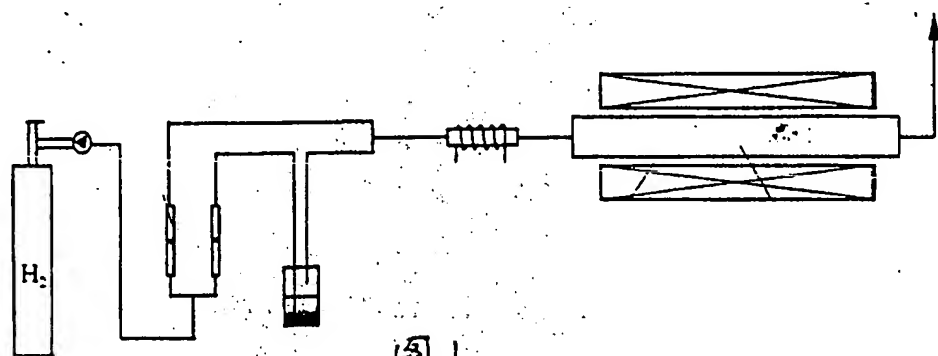


图 1

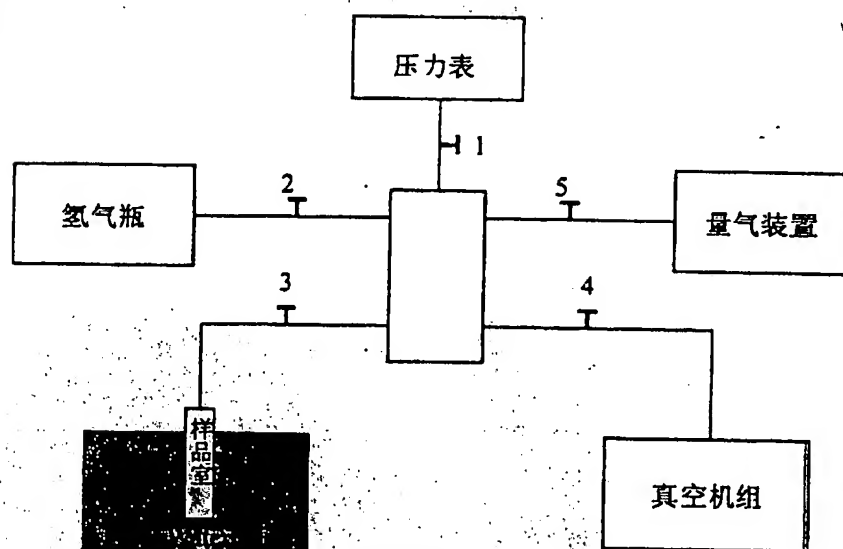


图 2

10mm



图 3



图 4



图 5

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[71]申请人 中国科学院金属研究所
地址 110015 辽宁省沈阳市沈河区文化路 72 号
[72]发明人 成会明 范月英 魏永良 吕曼琪
刘 敏 苏 革 沈祖洪

[74]专利代理机构 中国科学院沈阳专利事务所
代理人 张 晨

权利要求书 1 页 说明书 4 页 附图页数 2 页

[54]发明名称 一种纳米碳纤维储氢材料的制备方法

[57]摘要

一种纳米碳纤维储氢材料的制备技术,制备出的纳米碳纤维直径在 5~200 nm,以苯、CH₄、C₂H₂为碳源,以二茂铁、Ni(Co)₄为催化剂,以氢、氩、氮气为载气,其特征在于:以含硫化合物如噻吩、H₂S 为生长促进剂,并且控制碳源与载气的摩尔比在 0.08~0.18,碳与硫摩尔比为 700~1000:1,催化剂与碳源的摩尔比为 0.008~0.015;将含硫化合物碳氢化合物与催化剂在气态下充分混合,被载气匀速带入反应区,在反应区中保留 0.5~0.075S,在 1373K~1473K 下生长纳米碳纤维。本发明可以制备出大量储氢量大、性能稳定的储氢材料,且该方法简便易行,适合工业化生产。

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权 利 要 求 书

1. 一种纳米碳纤维储氢材料的制备技术, 制备出的纳米碳纤维直径在5~200 nm, 以苯、 CH_4 、 C_2H_2 为碳源, 以二茂铁、 $\text{Ni}(\text{Co})_4$ 为催化剂, 以氢、氮、氮气为载气, 其特征在于: 以含硫化合物如噻吩、 H_2S 为生长促进剂, 并且控制碳源与载气的摩尔比在0.08~0.18, 碳与硫摩尔比为700~1000:1, 催化剂与碳源的摩尔比为0.008~0.015; 将含硫化合物碳氢化合物与催化剂在气态下充分混合, 被载气匀速带入反应区, 在反应区中保留0.5~0.075 S, 在1373K~1473K下生长纳米碳纤维。
2. 按照权利要求1所述纳米碳纤维储氢材料的制备技术, 其特征在于: 含硫化合物为噻吩, 碳源为苯时, 当噻吩溶于某溶液中, 噻吩重量浓度0.05~1.0%。
3. 按照权利要求1所述纳米碳纤维储氢材料的制备技术, 其特征在于: 当含硫化合物为 H_2S 时, H_2S 进入反应区的量为0.5~1 ml/min。

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